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Characterisation of the torrefaction of beech wood using NIRS: Combined effects of temperature and duration

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ABSTRACT

A new approach is proposed to retrace the combined effects of temperature and duration within the thickness of heat-treated *Fagus sylvatica* wood. Torrefaction is a mild pre-treatment of biomass carried out at 200–300 °C to improve its properties for pulverized systems such as gasification. The properties of wood treated at high temperature are closely related to chemical modifications induced by temperature levels and treatment duration. This study involved the spectral analysis of solid wood in the near infrared range with the aim of developing a predictive model for process assessment. Samples of beech wood were used for calibration under high temperature conditions of 220, 250 and 280 °C for 1 and 8 h. For prediction, a 50-mm thick solid piece of wood was treated at 250 °C for 3 h. It was demonstrated that it is possible not only to distinguish between wood samples that have undergone different heat treatments, but also to retrace the thermal history of a piece of wood. Statistical processing showed the compensatory effects of temperature and duration, along with the existence of an exothermal reaction in the solid piece of wood. It should thus be possible to ensure cheaper and faster quality control in continuous torrefaction processes.

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1. Introduction

Biomass can be used to produce energy by various technologies: thermochemical, biological or chemical processes [1]. However, using raw biomass as fuel has certain drawbacks (low calorific value, high moisture content, hygroscopic nature). Biomass torrefaction is a pre-treatment carried out at 200–300 °C. The resulting decomposition reaction causes biomass to lose its tenacious and fibrous structure [2]. Such changes make torrefied biomass very attractive for use in pulverized systems, such as gasification. However, the torrefaction process involves heating biomass by an external energy source and is only worthwhile when it helps to reduce the cost of the overall biomass-to-energy production chain [3]. A major challenge is therefore to control biomass quality through torrefaction parameters such as time and temperature. Near Infrared Spectroscopy (NIRS) is a rapid, non-destructive analysis method that is increasingly being used in industry, especially the agrifood, chemical and textile industries. This technology has been used over the past 10 years in the wood industry to determine the amounts of constituent components in wood (lignin, cellulose, hemicelluloses,

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Table 1 – Number and nomenclature of treated samples.

T (°C)/t (h)	1 h	8 h
220 °C	H1–H10	H31–H40
250 °C	H11–H20	H41–H50
280 °C	H21–H30	H51–H60

extractives, etc.) [4,5]. Recent studies have shown that this method can also be calibrated to determine certain physical (such as humidity and density), mechanical and energy properties of wood [6]. The results obtained demonstrate that NIRS can be usefully employed to predict these characteristics, which are strictly dependent on the chemical composition of the wood [7,8].

The properties of wood treated at high temperature are closely related to chemical modifications induced by temperature conditions and treatment duration [9–11]. Our study involved the spectral analysis of solid wood in the near infrared, with the aim of developing a mathematical model able to determine the combined effects of temperature levels and duration applied to wood. This study was based on the hypothesis that the chemical composition of wood is modified by a cumulating effect of time and temperature. If that

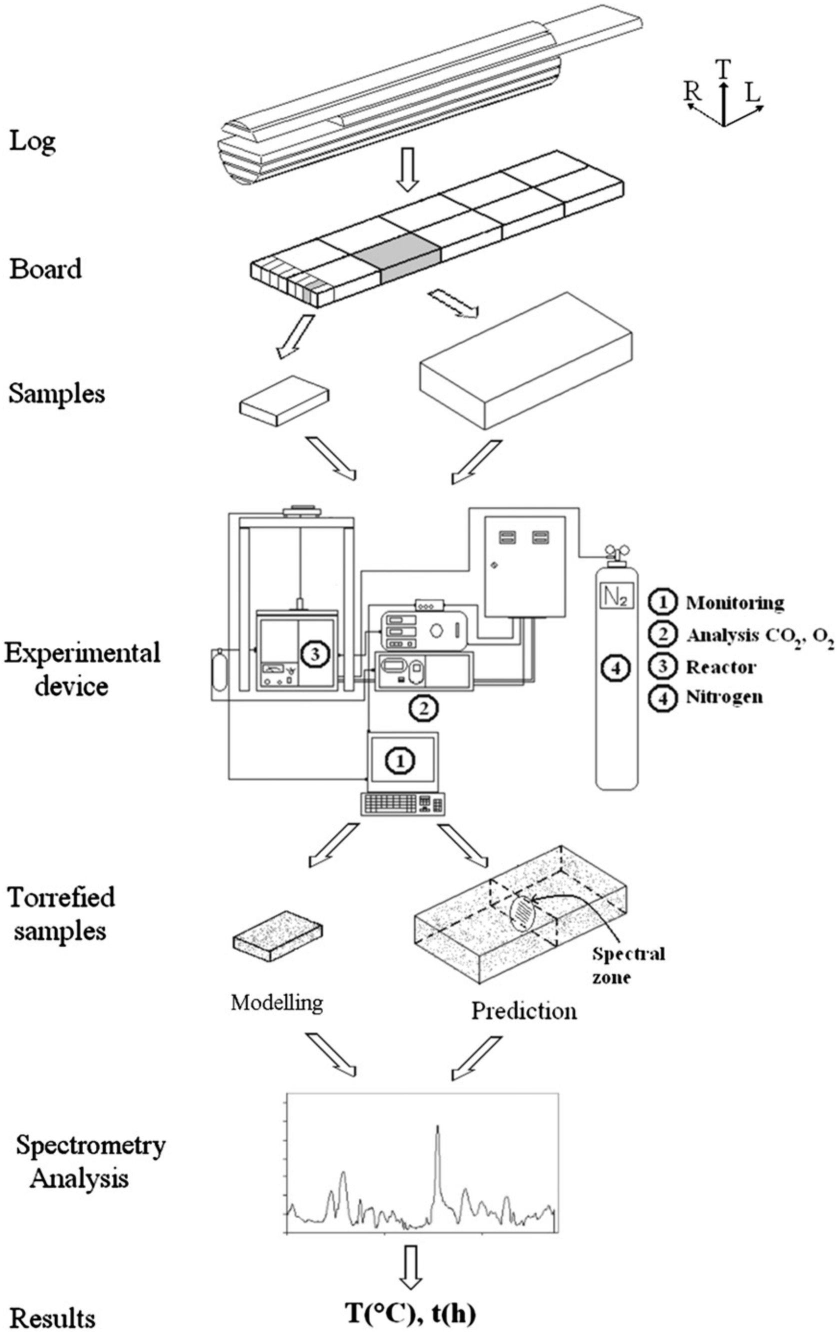


Fig. 1 – Sample preparation, heat treatment and spectrometric analysis.

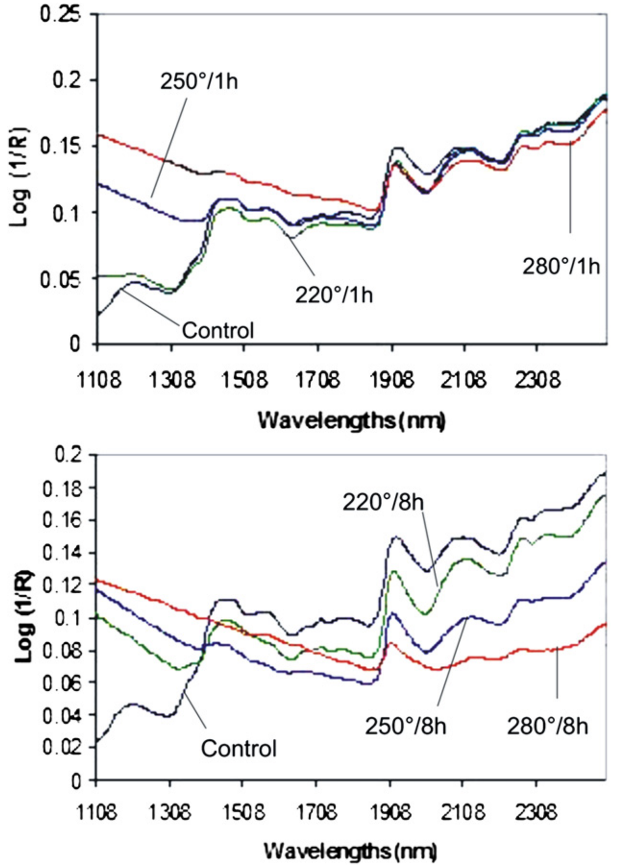


Fig. 2 – Spectra, means of 10 samples per temperature treatment for 1 h and 8 h.

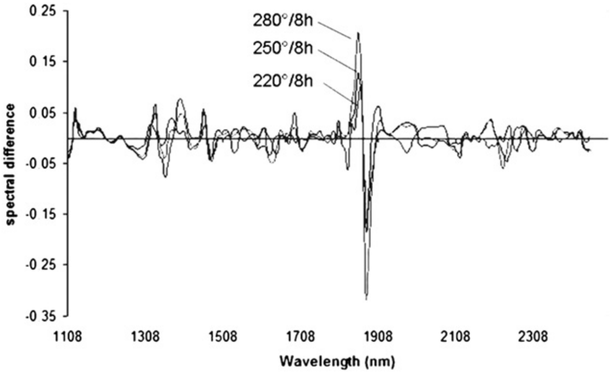


Fig. 4 – Differences in spectra for each experiment depending on treatment temperature and duration.

hypothesis is true, then it is possible to characterise samples according to their spectral fingerprint [12].

2. Methods

2.1. Materials

A key challenge when working with biomass is the biological nature of the raw materials. Their composition varies with species, season, and the various effects of post harvesting. Good sampling is an indispensable preliminary to any serious study of such material [13]. In this study, we selected a single tree (*Fagus sylvatica* L.) from a forest belonging to ENGREF. Beech logs were sawn into 50 mm-thick and quartersawn boards. They were then dried to an average humidity of ca. 12%. For comparative studies on the effects of temperature level and treatment duration, the wood samples were taken from a single longitudinal section from heartwood in order to limit the natural variability of wood and thus guarantee good reproducibility of the results. Sample dimensions for calibration were 20 mm × 12 mm × 3 mm (L, R, T) before treatment. The limited thickness was chosen to reduce the time constant of thermal diffusion, thus ensuring good uniformity during treatment throughout the section. On the other hand, a much thicker sample was used for prediction, measuring 300 mm × 150 mm × 50 mm.

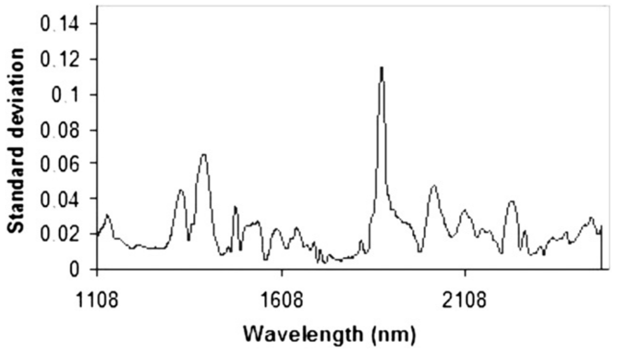


Fig. 3 – Standard deviation for the 65 samples (first derivation of spectra).

2.2. Heat treatment

The temperature levels chosen for the thermal treatments ranged from 220 to 280 °C, in an inert atmosphere (nitrogen). Wood properties vary significantly over this large range of temperatures [14]. Higher temperatures confer greater durability to wood, but also have a detrimental effect on certain mechanical properties. In contrast, lower temperatures lead to a less severe decrease in resilience. The database for calibration was constructed from tests using 60 samples on which three temperature levels and two treatment durations were tested (a total of six treatments). Each treatment was preceded by a 30-min drying phase at 110 °C. The heating rate was 5 °C min^{-1} for all treatments. Finally, we wanted the temperature history of the wood sample to be very close to that of the set temperature acting on the gas flow. This was ensured by a high heat transfer coefficient at the interface (using a copper sample of similar geometry, the average heat transfer coefficient was found to be 28 W $\mathrm{m}^{-2}\ {}^{\circ}\mathrm{C}^{-1}$) and by choosing a small sample thickness to reduce the time constant related to thermal diffusion in wood. This time constant τ reads as:

$$\tau = h^2 \rho C_p / \lambda [\mathrm{s}] \tag{1}$$

Table 2 – Groups formed depending on the number of classes required.

Class number	Groups obtained					
	C1	C2	C3	C4	C5	C6
6	250/1 h, 220/8 h	250/8 h	220/1 h	280/8 h	280/1 h	Control
5	250/1 h, 220/8 h	220/1 h, control	280/8 h	280/1 h	250/8 h	
4	250/1 h, 220/8 h, 250/8 h	280/1 h	280/8 h	220/1 h, control		
3	250/1 h, 220/8 h, 250/8 h, 280/1 h	280/8 h	220/1 h, control			
2	250/1 h, 220/8 h, 280/1 h, 250/8 h	Control, 220/1 h, 280/8 h				

In Equation (1), h is the half-thickness of the sample (m), ρ the wood density (kg m^{-3}), C_p the specific heat capacity of wood (J kg^{-1} k^{-1}) and λ the thermal conductivity of wood (J s^{-1} m^{-1} k^{-1}). Using usual values for wood ($\rho = 500$ kg m^{-3}, $C_p = 1250$ J kg^{-1} k^{-1} and $\lambda = 0.15$ J s^{-1} m^{-1} k^{-1}) and with a total thickness of 3 mm, the time constant τ was less than 10 s. This value was very small relative to the treatment duration, thereby ensuring uniform treatment throughout the section.

The number and nomenclature of samples per treatment are given in Table 1. We used the methodology described in Rousset et al. [15].

2.3. Spectrometric analysis

The spectra of the samples were obtained using diffuse reflectance on the wood in a Direct Contact Food Analyser (DCFA). Data were obtained for wavelengths between 400 nm and 2500 nm (in 2 nm increments), on a NIRSystems 6500 Foss spectrometer. Measurements were first taken on the ceramic reference (32 readings), followed by 32 readings on the sample. The absorbance spectrum, log (1/R) = f (λ nm), was obtained using these measurements (1 being the ceramic reference and R the reflectance of the sample for each wavelength). In order to adapt the spectrophotometer to the dimensions of the samples, we reduced the measuring window to 3 mm × 9 mm with a piece of aluminium foil. Two spectra were obtained for each sample (within an hour of each other), and the average of the two was recorded. All the spectral measurements were carried out according to the radial tangential (RT) plan (Fig. 1).

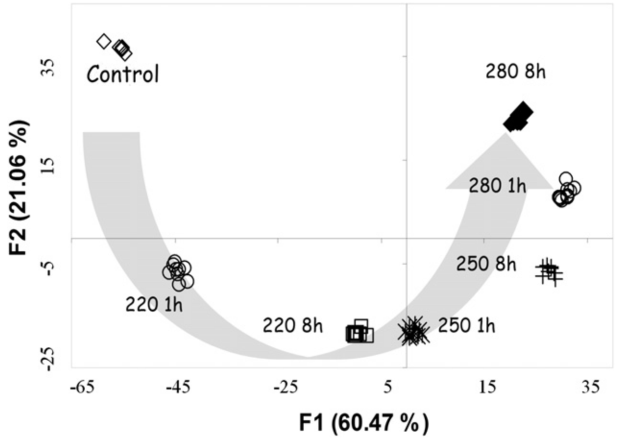


Fig. 5 – Scatter plot of the sample scores for the first two discriminant factors. The points are clustered into groups situated along a pathway which separates the different treatments according to treatment severity, from the mildest through to the harshest treatment as indicated by the arrow. It can be seen that the combined duration/temperature effect leads to the same chemical modifications.

3. Results and discussion

3.1. Spectral profiles

Observation of the raw spectra in the form of log (1/R) according to wavelength revealed differences for the following peaks (Fig. 2):

- 1212 and 1368 nm: disappearance after 200 °C/1 h (flatter spectrum after this)
- 1446–1476 nm: present from 220 to 250 °C/1 h then disappearance above 220 °C/8 h
- 1580 nm: disappearance above 250 °C/1 h
- 1722 nm: present from 220 to 250 °C/1 h and 220 °C/8 h
- 1900–1950 nm: steady decrease as temperature was increased with 8 h treatments
- 2062–2140: steady decrease with treatment
- 2270 nm: steady decrease with very high treatment, 280 °C/8 h.

It was possible to identify the most variable spectral bands (Fig. 3) from the standard deviation for each wavelength observed on the 65 samples. The peaks at 1138, 1336, 1400, 1884, 2030 and 2242 nm were thus identified as corresponding

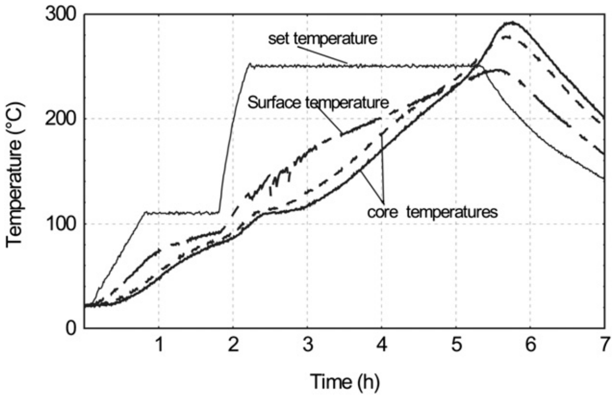


Fig. 6 – Temperatures recorded at three points in one sample of solid wood: surface (2 mm), and in the core (12 and 25 mm). Note that, due to exothermic reactions, the core temperature rises above the external set temperature.

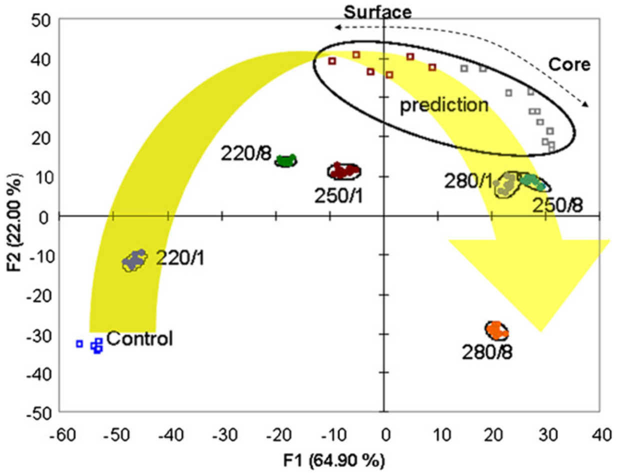


Fig. 7 – Discriminant analysis of the 65 spectra from the calibration samples and the 17 spectra from the solid wood sample. Treatments are clearly separated and a distinct progression is observed, from the mildest to the harshest treatments, as indicated by the arrow. Symmetry in the solid sample, from the surface to the core of the sample, can also be seen.

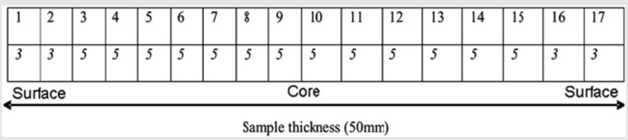
to the principal variations observed for the different treatments and for the control. By representing the spectra of the 65 samples in the form of the first derivative of the log (1/*R*), the differences between the spectral profiles of the treatments compared to the control were clear. Reproducibility was good for the spectra of the samples per treatment, demonstrating that the samples represented the treatments well.

These results tallied with previously published results [16]. It is well known that macromolecules (cellulose, hemicellulose and lignins) are degraded during heat treatment by the combined effect of temperature and treatment duration. Of all the wood polymers, hemicelluloses are the most unstable with respect to temperature [17]. This highly reactive heteropolymer is easily depolymerised at temperatures between 200 and 230 °C [18]. Xylans, which are plentiful in deciduous trees, are the most reactive and are very susceptible to degradation reactions and to dehydration between 200 and 260 °C [19]. They are the main source of volatile products (mostly furans and acetaldehyde) and play an important role in the initiation and propagation of pyrolysis reactions. The sensitivity of deciduous trees to increased temperature is directly related to their arabinose or uronic acid content, or the degree to which their hemicellulose presents substitutions of acetyl or 4-O-methyl groups [20,21]. These observations can be partially explained by combining two or more different analytical techniques [22].

Table 3 – Attribution of the 17 spectra from the solid wood sample to the calibration group.

Treatment	Group	Number of samples
220°/1 h	1	5 (Controls)
220°/8 h	2	0
250°/1 h	3	4
250°/8 h	4	0
280°/1 h	5	13
280°/8 h	6	0

Table 4 – Groups to which the spectra of the solid wood sample were attributed according to their position in the wood. The first line represents the number of the spectral sample (1 and 17 being the outermost spectra), the second line represents the calibration groups to which they were attributed. The highest temperatures corresponded to positions 3–15.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3	*3*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*3*	*3*

Surface Core Surface

Sample thickness (50mm)

The second major modification concerns cellulose. The relative thermal stability of cellulose is due to the highly structured character of cellulose fibrils, namely its crystalline part. The loss of certain mechanical properties in heated wood appears to be due to the simultaneous breakage of the glucosidic bonds between glucose monomers and of inter- and intra-molecular hydrogen bonds [23]. This weakness is accentuated by the presence of sugars, such as galactose, mannose and xylose, within the fibres [24]. Regarding the crystalline structure of cellulose, diverse hypotheses have been put forward [25]. Research has demonstrated that continuous or intermittent heat treatments have the same effect on the degree of cellulose crystallinity [26]. Compared to the highly micro-crystalline part, it seems that the amorphous regions are more reactive, the less ordered molecules being more readily degradable [27].

For lignins, heat treatment does not modify the nature of the radicals formed, but increases stationary concentration, which depends on the tree species. This increase can happen in two ways: either by direct thermal degradation of the phenolic components of the wood, or by the degradation of hemicelluloses, with the formation of radical species which then strip hydrogen from the phenolic components. This latter hypothesis highlights the role played by lignins and extractives in the chemical processes that intervene in the thermal degradation of wood, results that have been confirmed in recent studies [15]. The percentage of Klason lignin in the total weight increases with the severity of the heat treatment. The coefficient of lignin enrichment in heated beech wood demonstrated that a duration of 1 h at 220 °C had little effect, whereas lignin content doubled after 8 h treatment. In the most severe treatment (8 h at 280 °C) Klason lignin content in the sample was multiplied by almost 3.4. Taken together, these results highlight the ability of lignins to withstand the heat treatment applied, which explains their increase in relative content compared to less resistant wood components.

The differences between the mean spectrum of the control and the mean spectra of the various treatments were in fact progressive and corresponded to the previously identified

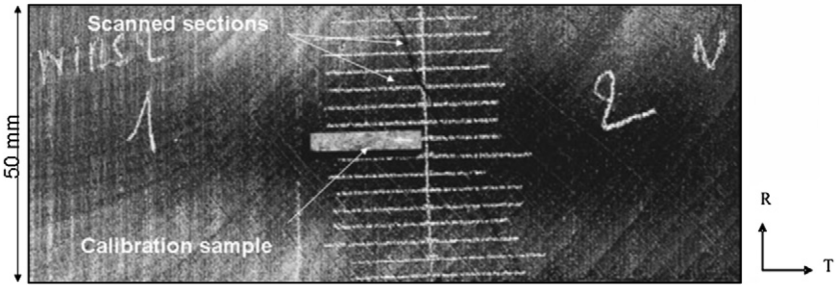


Fig. 8 – Significant differences throughout the thickness of the wood can be observed. As can the symmetry of the treatments. The pale zones represent low temperature treatments and the dark zones higher temperatures.

peaks. For the 1-h treatments, the spectral profiles were similar to that of the control. They displayed the same variations, the only difference being that the peaks were more or less marked, varying according to the temperature used. For the 8-h treatments, the differences were more obvious. This clearly illustrates the modifications generated by treatment duration (Fig. 4).

3.2. *Statistical analysis*

The algorithm of dynamic scatter was applied to all 65 spectra obtained from the samples (control and treatments) in the form of a primary derivative of the spectra after *SNVD* type correction of light scattering. After 38 iterations, the algorithm clearly identified a stable and strong form corresponding to the 7 classes. The classes were thus aligned in increasing order, starting from class 7 (control), then in the following order: (220/1 h), (220/8 h), (250/1 h), (280/8 h), (250/8 h) and (280/1 h). Distinct groups were identified according to their spectral fingerprints. For example, treatments at 220 and 250 °C for 8 h and 1 h respectively generated similar transformations. By changing the number of classes to be obtained, it was possible to identify strong 'sub-structures', i.e. groups within which spectral variance were small. When the number of classes required was reduced from 6 to 2, we obtained the results shown in Table 2. It can be seen that the samples were grouped in pairs: 250/1 h, 220/8 h and 280/1 h, 250/8 h. This unsupervised approach also revealed the close resemblance of the control spectra and those from the 220 °C/1 h treatment. This would suggest that this treatment had relatively little consequence for the chemical constitution of the wood, but modifications had indeed taken place since the control could be distinguished from this treatment in stable form when the analysis was raised to 7 classes.

A Discriminant Factorial Analysis (DFA) on the 65 spectra revealed relationships between a qualitative character (belonging to a group) and a set of quantitative explanatory characters. A DFA was chosen because it responds to two objectives: obtain the best possible separation between groups of individuals, and assign new individuals to the group to which they are closest. This approach was applied to ten principal components (PCs) from the spectral data. The first two discriminant factors explained 55% and 45% of the total variance respectively. 100% classification was obtained. An analysis of the correlations between the chosen principal components and the discriminant axes made it possible to identify those PCs that participated most in the construction of the axes. Hence, PC1 was found to be correlated to the 2nd axis ($r^2 = -0.76$), PC2 was correlated to the 1st axis ($r^2 = -0.70$), PC4 to the 1st axis ($r^2 = -0.30$), PC5 to the 2nd axis ($r^2 = -0.035$) and PC10 to the 1st axis ($r^2 = -0.32$). Fig. 5 shows the first discriminant function. Clusters of points correspond to treatments; they are clearly separated and situated along a curve, according to the severity and duration of heat treatment. This analysis confirmed the homogeneity of the heat treatment applied to the samples and the compensation effect of temperature and duration.

3.3. *Prediction*

We focussed on gaining a clearer understanding of the homogeneity or heterogeneity of the treatment within a piece of solid wood. To do this, we used a thick sample of wood (50 mm), to which we applied a set temperature so as to create a degradation gradient throughout the thickness of the wood. As seen in Fig. 6, a temperature inversion was observed at the core of the wood, with temperatures rising above the external temperature, reaching maximum values close to 300 °C. These phenomena have been observed before and commented on by Rousset et al. [28].

A second principal component analysis (PCA) was carried out on the spectral data of the 65 samples that had been used for calibration (marked as 'model' on the graph) and the 17 spectra of the 50-mm sample of solid wood (marked 'prediction'). We removed the visible spectra, as for calibration, so as to discriminate between samples solely on the basis of chemical composition and not on the basis of colour. We then carried out a discriminant analysis using the first 10 PCs produced by the PCA in order to attribute each of the 17 spectra from the solid wood sample to the groups plotted from calibration samples (Fig. 7).

The 17 spectra from the solid wood sample were assigned to groups by the discriminant model as shown in Table 3. Perfect symmetry can be observed with the higher temperatures within the wood sample (group 5). It is also evident that the behaviour of the controls resembled that of the calibration samples treated at 250 °C/1°h. This indicates that the samples that underwent mild treatment did not undergo significant chemical modification, corroborating previous studies [29].

Two groups were distinguished among the spectra from the heat-treated sample of solid wood. These groups could be situated within the wood sample (Table 4).

The spectral analyses showed that the severe heating conditions of the treatment did in fact result in significant differences throughout the thickness of the wood. The DFA suggested that the core of the sample underwent treatment that was equivalent to that undergone by the calibration samples treated at 280°/1 h. This more severe treatment obtained in the core of the sample obviously resulted from exothermic reactions. Indeed the temperature measurements (Fig. 6) showed that a peak of 285 °C was attained for a period of 30 min, with the temperature declining towards the surface of the wood. These measured temperatures mirrored the model's prediction. Moreover, the symmetry of the treatments can be seen in the Fig. 8, where the pale zones represent low temperature treatments and the dark zones higher temperatures.

4. Conclusions

The results presented here indicate that near infrared diffuse reflection spectrometry is a technique that can be adapted to the rapid measurement of native wood and thermally treated wood. The small sizes of the samples used for calibration led to uniform treatment. The statistical analysis revealed the compensatory effect of treatment temperature and duration. Thus, at constant temperature, it would be possible to ascertain a treatment duration. The thick sample was treated in such a way as to obtain a difference in treatment history between the surface and core. Recordings during treatment revealed a symmetric distribution of temperatures with a peak at 285 °C at the core. The predictive model revealed that symmetry by associating the spectra with the temperature/duration pairs of 250 °C/1 h for the peripheral zones and 280 °C/1 for the core.

Finally, it should be remembered that, in this study, great care was taken to avoid variability in the material, thereby focussing the study on the effect of temperature level and duration (same tree, same longitudinal section, small thickness). In the future, for the constructed models to be robust, the natural variability of wood will have to be taken into consideration; both the within-tree variability of chemical composition depending on the position in the tree, and the between-tree variability of wood from the same species.

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